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Cobalt catalysts for the conversion of CO₂ to light hydrocarbons at atmospheric pressure†Cite this: *Chem. Commun.*, 2013, **49**, 11683Received 5th September 2013,
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A series of cobalt heterogeneous catalysts have been developed that are effective for the conversion of CO₂ to hydrocarbons. The effect of the promoter and loadings have been investigated.

One of the “holy grails” for the catalysis community for the 21st century remains the development of robust and cheap systems for the upgrading of CO₂. With the dwindling supply of oil derived chemical feedstocks coupled with uncertainties of supply, now is unequivocally the time to act.¹ The “shale-gas boom” in the US (and Europe) remains, to date, a temporary life-line rather than a long-term solution. Therefore, it is of paramount importance to find a sustainable alternative. We and several other groups across the world have already taken up this research challenge – mainly utilising iron promoted systems for the conversion of CO₂ to hydrocarbons (HCs).² Far less attention has been applied to cobalt containing catalysts; this is largely due to their preference to form CH₄.³ One of the first examples of this catalysis was in 1950 by Miller with a series of activated cobalt systems.⁴ In more recent years examples of active catalysts include those of Somorjai who have prepared cobalt nanoparticles on MCF-17 mesoporous silica with the major products being CH₄ and CO.⁵ It is observed that platinum can act as a promoter for such processes. Willauer and co-workers have investigated a Co–Pt/Al₂O₃ system for the conversion of CO₂ to HCs.⁶ The lowest selectivity to CH₄ being 93.1% (*T* = 220 °C, *P* = 275 psi, H₂:CO₂ 1:1) higher selectivities towards CH₄ were observed with H₂:CO₂ ratios of 2:1 and 3:1. It was hypothesised that changing this ratio lowered the methanation ability of the catalysts and conversely favoured chain growth.

In this paper we report the utilisation of a new series of cobalt-containing heterogeneous catalysts for the conversion of CO₂ to HCs at atmospheric pressure. The catalysts were prepared by the wet impregnation of the appropriate metal salts on the silica support.[†] The catalysts were characterised by TEM, SEM, XPS and pXRD.[†]

From XPS and pXRD the cobalt is present as Co₃O₄. Initial catalytic results are shown in Table 1, the cobalt only system (entry 1) gave good conversion but to predominately CH₄, analogous to literature precedent.^{4–6} It has been shown that the addition of a noble metals has a beneficial effect upon the catalysis.⁸ It has also previously been shown that adding alkali metals with cobalt increases selectivity to heavier HCs (for traditional FT reaction).⁹ Furthermore, in traditional FT catalysis the olefin–paraffin ratio increases with addition of alkali metals.¹⁰ Thus, we tested a range of Co:K systems Table 1 entries 2–9 with palladium present to aid CO production and potassium to increase selectivity to heavier HCs. A cobalt loading of 20 wt% was found to be optimal in terms of conversion but with higher loadings producing lower quantities of CH₄. Increasing potassium loading was found to reduce selectivity towards CH₄ and led to an increased yield of heavier HCs, this occurs at the cost of conversion with high potassium loadings leading to lower CO₂ conversion. Comparing entries 1 vs. 4 vs. 9 it is clear that for this system there is no advantage, in-terms of selectivity, adding palladium to the catalyst. Comparing entries 1 and 9 there is a dramatic reduction in conversion, with a concurrent increase in selectivity to heavier HCs. As expected the palladium containing systems produced lower level of olefins, entry 4 vs. 9, compared to the potassium promoted system.

The pore diameter of the SiO₂ was varied (60, 250, 500 Å) Table 1 entry 4 (60 Å) vs. Table 2 entries 1 and 2. Generally as the pore diameter is increased the HC yield decreases, however a noticeable increase in selectivity away from CH₄ is observed. However, the same trend is not observed for the 20 wt%Co/1 wt%K/SiO₂ system. Noteworthy, is that the large pore diameter silica appears to facilitate the formation of slightly larger crystalline phases, which maybe related to the enhanced selectivity.^{†11} To assess the potential to scale-up this catalyst system a larger particle size support was utilised, Table 2 entry 3. There was a reduction in conversion compared to the 35–70 μm material (Table 1, entry 4) potentially due to diffusional effects; HC distribution was however observed to remain similar. The removal of all promoters, giving a 20 wt%Co/SiO₂-500 catalyst (Table 2 entry 8) resulted in almost exclusively CH₄ formation as observed with the use of 60 Å pore size silica (Table 1, entry 1) showing the use of larger pore size silica alone

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† Electronic supplementary information (ESI) available: Synthesis, characterisation details and tentative mechanism. See DOI: 10.1039/c3cc46791k

Table 1 Initial catalyst screen

| Entry | Catalyst ^a | Con. (%) | CO yield (%) | HC yield (%) | C ₁ | C ₂₌ | C ₂ | C ₃₌ | C ₃ | C ₄ | C ₅₊ |
|-------|---------------------------|----------|--------------|--------------|----------------|-----------------|----------------|-----------------|----------------|----------------|-----------------|
| 1 | 20 wt%Co | 67.4 | 2.8 | 64.4 | 99.7 | 0 | 0.3 | 0 | 0 | 0 | 0 |
| 2 | 20 wt%Co/1 wt%Pd | 50.7 | 3.2 | 47.5 | 99.7 | 0 | 0.3 | 0 | 0 | 0 | 0 |
| 3 | 10 wt%Co/1 wt%Pd/1 wt%K | 36.4 | 2.9 | 33.5 | 97.0 | 0 | 2.7 | 0 | 0.3 | 0 | 0 |
| 4 | 20 wt%Co/1 wt%Pd/1 wt%K | 63.4 | 8.8 | 54.6 | 93.2 | 0 | 5.4 | 0 | 1.2 | 0 | 0 |
| 5 | 40 wt%Co/1 wt%Pd/1 wt%K | 39.1 | 3.7 | 35.4 | 91.6 | 0 | 6.4 | 0 | 1.7 | 0.3 | 0.1 |
| 6 | 20 wt%Co/1 wt%Pd/0.5 wt%K | 62.8 | 9.6 | 53.3 | 89.5 | 0 | 7.3 | 0 | 2.6 | 0.6 | 0 |
| 7 | 20 wt%Co/1 wt%Pd/1.5 wt%K | 59.1 | 9.6 | 49.5 | 77.2 | 0 | 10.6 | 0 | 7.6 | 3.1 | 1.5 |
| 8 | 20 wt%Co/1 wt%Pd/3 wt%K | 43.2 | 10.5 | 32.7 | 70.1 | 0 | 10.9 | 0 | 10.3 | 5.2 | 3.6 |
| 9 | 20 wt%Co/1 wt%K | 36.1 | 6.1 | 29.9 | 54.7 | 2.0 | 11.5 | 10.7 | 3.8 | 2.5 | 9.5 |

^a Metal nanoparticles are supported on SiO₂, pore diameter 60 Å. Test conditions: temperature, 643.15 K; pressure—atmospheric; H₂/CO₂ ratio 3 : 1 results were calculated after at least 5 hours on stream. Note: blank silica was tested but showed no observable catalytic activity.

Table 2 Effect of noble metal, pore size and additional promoter on catalytic efficiency

| Entry | Catalyst ^a | Con. (%) | CO yield (%) | HC yield (%) | C ₁ | C ₂₌ | C ₂ | C ₃₌ | C ₃ | C ₄ | C ₅₊ |
|-------|---|----------|--------------|--------------|----------------|-----------------|----------------|-----------------|----------------|----------------|-----------------|
| 1 | 20 wt%Co/1 wt%Pd/1 wt%K_250 | 44.9 | 3.0 | 41.9 | 76.9 | 0 | 13.0 | 0 | 7.0 | 2.0 | 1.1 |
| 2 | 20 wt%Co/1 wt%Pd/1 wt%K_500 | 41.6 | 5.7 | 36.8 | 62.8 | 0 | 17.0 | 0 | 11.6 | 4.7 | 3.7 |
| 3 | 20 wt%Co/1 wt%Pd/1 wt%K_60 ^b | 45.7 | 3.6 | 42.2 | 91.6 | 0 | 6.3 | 0 | 1.6 | 0.4 | 0.1 |
| 4 | 20 wt%Co/1 wt%Pt/1 wt%K_500 | 36.5 | 7.6 | 28.9 | 52.4 | 0.3 | 15.5 | 2.9 | 9.9 | 6.9 | 12.1 |
| 5 | 20 wt%Co/1 wt%Ru/1 wt%K_500 | 45.1 | 5.7 | 39.4 | 60.2 | 0.5 | 13.3 | 6.7 | 5.9 | 7.0 | 6.5 |
| 6 | 20 wt%Co/1 wt%Pd/1 wt%Li_500 | 39.5 | 7.6 | 31.9 | 69.5 | 0 | 18.9 | 0.2 | 6.9 | 2.2 | 2.4 |
| 7 | 20 wt%Co/1 wt%Pd/1 wt%Na_500 | 41.9 | 8.5 | 33.4 | 60.7 | 0 | 14.9 | 2.0 | 8.5 | 4.7 | 9.2 |
| 8 | 20 wt%Co_500 | 64.3 | 4.3 | 60.0 | 98.2 | 0 | 1.8 | 0 | 0.1 | 0 | 0 |
| 9 | 20 wt%Co/1 wt%Li_500 | 39.3 | 8.4 | 30.9 | 74.3 | 0.6 | 14.8 | 2.6 | 4.7 | 2.5 | 0.6 |
| 10 | 20 wt%Co/1 wt%Na_500 | 51.2 | 11.1 | 40.1 | 53.7 | 2.1 | 13.4 | 11.1 | 5.1 | 8.2 | 6.4 |
| 11 | 20 wt%Co/1 wt%K_500 | 47.6 | 8.1 | 39.5 | 60.4 | 1.4 | 13.0 | 9.0 | 5.2 | 6.6 | 4.4 |
| 12 | 20 wt%Co/1 wt%Mo_500 | 64.8 | 4.2 | 60.7 | 94.7 | 0 | 5.0 | 0 | 0.3 | 0 | 0 |
| 13 | 20 wt%Co/1 wt%Cr_500 | 60.9 | 13.9 | 47.1 | 98.2 | 0 | 1.6 | 0.1 | 0.1 | 0.1 | 0 |
| 14 | 20 wt%Co/1 wt%Mn_500 | 62.0 | 4.3 | 57.7 | 97.9 | 0 | 2.0 | 0 | 0.1 | 0 | 0 |
| 15 | 20 wt%Co/1 wt%Na/1 wt%Mn_500 | 42.7 | 8.4 | 34.3 | 72.4 | 0.8 | 13.1 | 4.4 | 4.9 | 3.5 | 1.0 |
| 16 | 20 wt%Co/1 wt%Na/1 wt%Mo_500 | 43.9 | 6.9 | 37.0 | 45.5 | 1.7 | 15.8 | 11.1 | 6.4 | 9.1 | 10.4 |

^a Metal nanoparticles are supported on SiO₂, _X where X is the pore diameter of the SiO₂. ^b SiO₂ particle size 1–2 mm (N.B. all other SiO₂ are in the range 35–70 µm). Test conditions: temperature, 643.15 K; pressure—atmospheric; H₂/CO₂ ratio 3 : 1 results were calculated after at least 5 hours on stream.

is not sufficient to significantly influence product selectivity. The 500 Å pore size SiO₂ material was taken forward and the noble and group 1 metal were systematically varied, Table 2 entries 4–7. Typically, the HC distribution obeyed the Anderson–Schulz–Flory distribution.[†]

The nature of the noble metal was varied (Table 2 entries 2 vs. 4 and 5). An increase in conversion is observed with the presence of ruthenium and CH₄ selectivity is also seen to decrease with selectivity to C₅₊ HCs almost doubling. Replacement of palladium with platinum led to a large decrease in selectivity towards CH₄ with C₅₊ selectivity increasing to ca. 12%. This improvement in selectivity occurs with only a slight decrease in conversion. The variation of alkali metal was investigated (entries 2 vs. 6 and 7). The lithium system performed worse both in terms of conversion and selectivity relative to the potassium promoted system. The sodium catalyst on the other hand gives greater selectivity to C₅₊ HCs with no decrease in conversion.

As with the analogues SiO₂_60 Å supported systems the removal of the noble metal to give alkali metal only promoted systems (Table 2 entries 9–11) still significantly outperformed the cobalt only system in terms of product selectivity. Conversion values recorded for the lithium catalyst with and without palladium remain very similar, however, both sodium and potassium systems show an increase in conversion in the absence of palladium, the opposite to that observed for the

SiO₂_60 Å systems (Table 1, entries 4 and 9). CH₄ selectivity is also observed to be lower for these two catalysts with the Co–Na catalyst performing best. In direct contrast to the noble metal promoted catalysts (Table 2 entries 2, 6 and 7) the systems promoted with only alkali metals show a high degree of selectivity towards olefins. The improved HC selectivity observed upon alkali addition has been attributed to an enhancement in surface to molecule charge transfer,¹² increasing CO binding strength and reducing the H₂ binding strength, thus, resulting in an increased chain growth probability and higher alkene selectivity.¹³

With results showing that the addition of expensive noble metals are not needed to obtain good product distributions some cheaper more abundant transition metal alternatives were also investigated. The addition of manganese to cobalt catalysts used for the CO-fed FT process has shown an increase in water–gas shift activity.¹⁴ Molybdenum has been shown to be active for the FT process itself and addition to cobalt based FT catalyst has resulted in an improved catalyst performance.¹⁵ The addition of small loadings of these metals along with chromium, whose addition has been shown to increase selectivity towards longer chained HCs with some cobalt based FT catalysts, were investigated (Table 2 entries 12–14).

A slight drop in conversion was observed upon the addition of chromium to the system combined with a higher selectivity to CO, this resulted in a reduced HC yield. Little effect on conversion



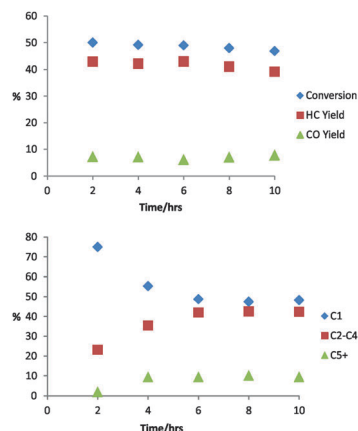


Fig. 1 Top: conversion vs. time plot for 20 wt%Co/1 wt%Na/1 wt%Mo_500. Bottom: selectivity vs. time plot for 20 wt%Co/1 wt%Na/1 wt%Mo_500.

and HC yield was observed with molybdenum and manganese addition. The chromium system showed little difference in CH_4 selectivity relative to the non-promoted cobalt system (Table 2 entry 8). A more significant decrease in CH_4 selectivity was obtained upon the addition of molybdenum and manganese. Molybdenum addition was found to be the most effective of the three transition metals tested although its promotional abilities pale in comparison to those obtained with the addition of alkali metals (Table 2 entries 9–11). The improvement observed upon the addition of molybdenum can likely be attributed to the suppression of CH_4 formation as observed with cobalt catalysts for FT catalysis.¹⁵

In order to ascertain if the promotional abilities of the alkali metal systems could be combined with the slight improvement observed with the manganese and molybdenum systems two catalyst systems were prepared containing a combination of 1 wt% sodium (the best performing alkali metal) with 1 wt% of each of the best performing transition metals (Table 2 entries 15 and 16). The combination of manganese and sodium as promoters shows a lower conversion than that observed for both the non-promoted system and the individually promoted systems. Product selectivity was observed to be intermediate between the sodium only and manganese only promoted system. The dual promotion with sodium and molybdenum proved far more successful. The catalyst gives a greater selectivity to heavier C_{5+} HCs similar to that observed for the Co–K–Pt system (Table 2 entry 4) however conversion was found to be higher. CH_4 selectivity was found to be 45.5%, the lowest observed for any of the catalyst systems tested. No change in cobalt binding energy was observed by XPS with sodium and molybdenum addition. However, the addition of molybdenum may favour the formation of alkylidene species, which are important in the chain growth mechanism.[†]

Catalyst pre-treatment for all tests reported so far consists of a 2 hour hydrogenation at 300 °C. In order to determine if conversion or selectivity could be improved further a longer pre-treatment was trialled. The H_2 flow was maintained for 15 h before reaction. The alkali metal containing catalyst systems studied required 4–5 h on stream before product selectivity stabilised. For the extended pre-treatment tests, the system

yielding the best HC distribution was chosen, 20 wt%Co/1 wt%Na/1 wt%Mo_500, Fig. 1. Conversion remained stable for the entirety of the time on stream with an average conversion of 48.6%, a 5% increase over that observed for the system after a 2 h reduction. There was no evident difference in the time taken for product selectivity to stabilise with the catalyst requiring 4–6 h to stabilise after both the 2 and 15 h pre-treatments. HC distribution showed very little difference with C_{5+} selectivity ~10% for the system with both pre-treatment times.

In conclusion a range of cobalt based catalysts were prepared and tested for their ability to hydrogenate CO_2 at atmospheric pressure. Conversion values although reduced upon the introduction of some promoters still compares favourably with other catalysts, even iron-based systems currently being studied for the process. Product selectivities significantly superior to other cobalt based catalyst reported from CO_2 hydrogenation are observed. Further studies are on-going to gain an understanding of silica pore size effects coupled with computational studies to gain further insight into the electronic effects of the promoters, specifically molybdenum and sodium, on the cobalt component.

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